High-Pressure Phase Equilibrium for Ethane + 2-Propanol at 308.15 K and 313.15 K

Daisuke Kodama, Masahiko Ogawa,[†] Tomoaki Kimura, Hiroyuki Tanaka, and Masahiro Kato*

Department of Materials Chemistry and Engineering, College of Engineering, Nihon University,
Koriyama, Fukushima 963-8642, Japan

Phase equilibria and saturated densities were measured at 308.15 K and 313.15 K with a static-circulation apparatus for ethane + 2-propanol at high pressures. An experimental apparatus equipped with three Anton Paar DMA 512S vibrating tube density meters had been previously developed for measuring vapor−liquid−liquid phase separation properties at high pressures. Coexisting phase compositions and saturated densities of each phase could be measured with the apparatus with a maximum temperature and pressure of 400 K and 20 MPa, respectively. For the present system, Kuenen et al. (*Philos. Mag.* **1899**, *48*, 180−203) had previously reported only the upper critical end point and the approximate lower critical end point. In the present study, the vapor−liquid equilibrium composition and saturated density of each phase were determined by gas chromatography and density measurements, respectively. Vapor−liquid−liquid equilibria was not observed in the present experiments. The experimental data obtained were correlated with equations of state.

Introduction

Phase equilibrium properties of mixtures at high pressures are required for practical uses such as the design and operation of separation equipment in the petroleum, natural gas, and related industries. Supercritical fluid extraction is now attractive as a separation technology.

Kuenen et al.[1] had previously reported only the upper critical end point (UCEP) as 317.15 K and the approximate lower critical end point (LCEP) range from 311.15 K to 315.15 K. Kuenen et al. further observed three layers at temperatures below 311.15 K down to about 298.15 K. Kuenen et al. suggested that the phase separation behaviors are probably due to impurities in 2-propanol. The authors did not find published vapor−liquid equilibrium (VLE) data for the ethane + 2-propanol system.

A static-circulation apparatus equipped with three density meters for measuring vapor−liquid−liquid equilibria (VLLE) at high pressures was described previously.[2] With this apparatus, VLE and their saturated densities were reported for carbon dioxide + ethanol[2] and carbon dioxide + 1-butanol[3] at high pressures. Phase equilibrium properties of ethane + methanol,[4] ethane + ethanol,[5] and ethane + 1-propanol[6] have been recently measured, including VLLE.

In the present study, the coexisting phase compositions and their saturated densities for the ethane + 2-propanol mixture at high pressures are measured at 308.15 K and 313.15 K, including in the critical region.

The phase equilibrium relations obtained in the present study are correlated with the Soave−Redlich−Kwong[7] (SRK) and pseudocubic[8] equations of state.

Experimental Section

Materials. Ethane was supplied by Takachiho Chemical Industrial Co. Ltd. with a guarantee of 99.9% purity. 2-Propanol was a special-grade reagent of Wako Pure Chemical Industries, Ltd. and was used without further purification. The purity of 2-propanol was determined to be 99.9% from gas chromatographic peak areas.

Apparatus and Procedures. The apparatus and experimental procedures[2] are the same as those described previously. The apparatus is a static-circulation type, which can operate to a maximum temperature and pressure of 400 K and 20 MPa, respectively, and has three Anton Paar DMA 512S vibrating tube density meters. The apparatus is immersed in a constant-temperature liquid bath controlled within ±0.01 K. The cell volume is approximately 320 cm^3. The coexisting phases were continuously recirculated through the sampling valves and density meters with the three magnetic circulation pumps. Temperatures were measured with a Hewlett-Packard 2804A quartz thermometer. Pressures were measured with a Ruska 2480-700 oil dead weight gauge and a Ruska 2439-702 pressure transducer. The equilibrium phase compositions were determined by using a Shimadzu GC-14A gas chromatograph equipped with a 3-m Porapak Q column. Helium was used as a carrier gas at a flow rate of 30 $cm^3 \cdot min^{-1}$. The injection temperature and column temperature were about 423 K and 403 K, respectively. The current value of a thermal conductivity detector (TCD) was 100 mA.

The samples, ethane and 2-propanol, were charged into the cell after the evacuation of the cell. The fluid in the cell was mixed with a magnetic-driven agitator. Each phase was circulated with its circulation pump. After a steady state was established for 2 or 3 h, the agitator and circulation pumps were stopped. After 1 h, the densities and the pressure were measured with density meters and a dead weight gauge, respectively. A sample of each phase was taken with a sampling valve and analyzed by gas chromatography after a circulation for 2 h in the sampling room.

Results and Discussion

Tables 1 and 2 present the experimental results of coexisting phase compositions and their saturated densities

---

* To whom correspondence should be addressed. Fax: (81)-24-956-8862. E-mail: mkatoh@chem.ce.nihon-u.ac.jp.
[†] Present address: Dai Nippon Printing Co., Ltd.

10.1021/je010324i CCC: $22.00

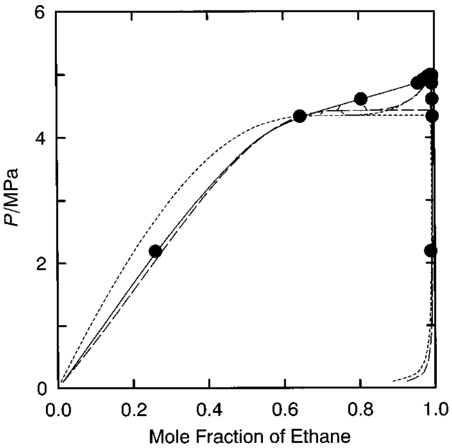

Figure 1. Phase equilibria for the ethane (1) + 2-propanol (2) system at 308.15 K: (—●—) this work; (- - -) pseudocubic equation of state ($k_{12} = 0.1055$); (···) SRK equation of state ($k_{12} = 0.0707$).

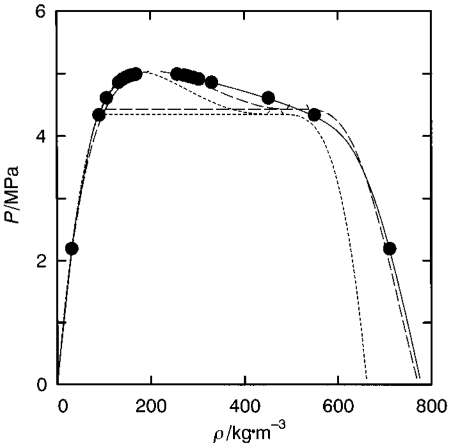

Figure 2. Saturated densities for the ethane (1) + 2-propanol (2) system at 308.15 K: (—●—) this work; (- - -) pseudocubic equation of state ($k_{12} = 0.1055$); (···) SRK equation of state ($k_{12} = 0.0707$).

Table 1. Saturation Pressure *P*, Liquid Mole Fraction *x*, Vapor Mole Fraction *y*, Liquid Density ρ_L, and Vapor Density ρ_V for Ethane (1) + 2-Propanol (2) at 308.15 K

P/MPa	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
2.191	0.260	0.990	711.2	31.9
4.336	0.644	0.996	550.6	91.1
4.609	0.806	0.995	452.3	106.9
4.858	0.957	0.994	331.0	133.0
4.912	0.971	0.993	303.3	142.5
4.936	0.978	0.993	292.1	148.5
4.958	0.983	0.992	280.2	155.1
4.972	0.986	0.992	273.3	160.0
4.990	0.990	0.994	257.4	169.8

for the ethane + 2-propanol system at 308.15 K and 313.15 K. Previously, VLLE phase separation was reported for ethane + 1-propanol by Kuenen et al.[1] However, VLLE phase separation was not observed in the present experiments for the ethane + 2-propanol system. The uncertainties of the experimental equilibrium composition, density, temperature, and pressure are ±0.001 mole fraction, ±0.1 kg·m^{-3}, ±0.1 K, and ±1 kPa, respectively.

Figures 1 and 2 respectively give the pressure−composition and the saturated density diagrams at 308.15 K. Figures 3 and 4 show the results at 313.15 K. In Figures 1−4, the solid lines denote the experimental smoothed curves drawn by considering the uncertainties of the experimental data.

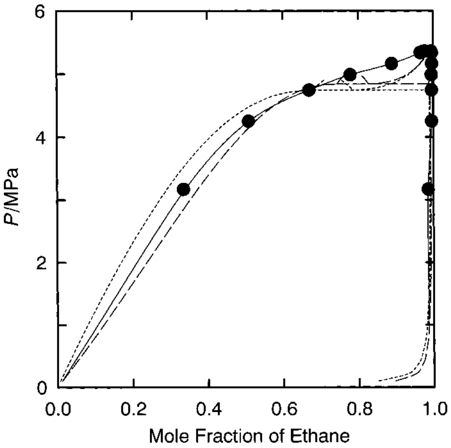

Figure 3. Phase equilibria for the ethane (1) + 2-propanol (2) system at 313.15 K: (—●—) this work; (- - -) pseudocubic equation of state ($k_{12} = 0.1097$); (···) SRK equation of state ($k_{12} = 0.0736$).

Table 2. Saturation Pressure *P*, Liquid Mole Fraction *x*, Vapor Mole Fraction *y*, Liquid Density ρ_L and Vapor Density ρ_V for Ethane (1) + 2-Propanol (2) at 313.15 K

P/MPa	x_1	y_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
3.169	0.336	0.984	673.9	49.5
4.251	0.509	0.995	606.7	79.5
4.744	0.670	0.995	537.3	101.3
4.985	0.779	0.995	465.1	117.6
5.162	0.890	0.996	383.9	135.7
5.335	0.966	0.996	283.3	179.0
5.353	0.974	0.995	259.9	196.9
5.357	0.978	0.994	249.3	202.0

Correlations

The experimental data obtained were correlated with the conventional SRK[7] equation of state and the pseudocubic[8] equation of state.

The pseudocubic[8] equation of state is expressed as follows:

$$P = \frac{RT}{V^* - b} - \frac{a}{V^{*2}}, \quad V^* = \frac{(V - \epsilon b)(V + \sigma b)}{V} \tag{1}$$

$$\epsilon = (1 - \theta)(\xi - 2), \quad \sigma = (1 - \theta)(\xi + 2) \tag{2}$$

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}}, \quad \theta = \frac{8Z_c}{3}, \quad Z_c = \frac{P_c V_c}{RT_c} \tag{3}$$

$$a = K_a a_c, \quad b = \frac{RT_c}{8P_c}, \quad a_c = \frac{27(RT_c)^2}{64P_c} \tag{4}$$

$$\ln K_a = S(1 - \sqrt{T_r}), \quad S = 1.1746 + 3.4539\omega \tag{5}$$

where P, R, T, V, Z, and ω denote respectively the pressure, gas constant, temperature, molar volume, compressibility factor, and acentric factor. K_a, S, a, b, ϵ, θ, σ, and ξ represent the parameters. The subscripts c and r denote the critical property and reduced property, respectively. The asterisk indicates the apparent value.

The following mixing rules were used, introducing binary interaction parameter k_{ij}:

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad b = \sum_i \sum_j x_i x_j b_{ij}, \quad \theta = \sum_i x_i \theta_i \tag{6}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j}, \quad b_{ij} = \frac{b_i + b_j}{2} \tag{7}$$

where x represents the mole fraction. The subscripts i and j denote the components.

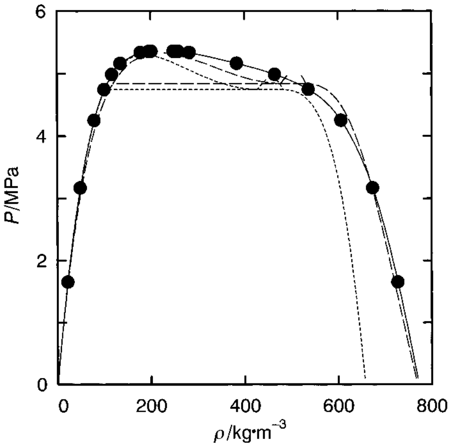

Figure 4. Saturated densities for the ethane (1) + 2-propanol (2) system at 313.15 K: (–●–) this work; (- - -) pseudocubic equation of state (k_{12} = 0.1097); (···) SRK equation of state (k_{12} = 0.0736).

The binary interaction parameter k_{12} was evaluated as 0.1055 at 308.15 K and 0.1097 at 313.15 K, from the present experimental bubble-point pressure data in the lower pressure regions for the SRK and the pseudocubic equations.

In the correlations, the critical values and acentric factors of ethane and 2-propanol were obtained from the work of Reid et al.[9]

Calculation results with the equations of state are shown in Figures 1–4. In Figures 1–4, the solid, dotted, and broken lines denote respectively the experimental smoothed data, the calculation results by the SRK equation, and the ones by the pseudocubic equation. In Figures 1–4, the horizontal lines denote the VLLE separation ranges calculated with the equations of state. As shown in Figures 1–4, the VLLE separations in the narrow composition ranges were calculated by the equations of state. The equation of state is generally applied for the VLE correlation, mainly for the pressure–composition behavior, not for the saturated vapor and liquid density behavior.

Conclusions

Phase equilibria and saturated densities for ethane + 2-propanol at high pressures were measured at 308.15 K and 313.15 K with a static-circulation apparatus. The experimental data obtained were correlated by the equations of state.

Acknowledgment

The authors thank Mr. Daisuke Fujita for his help in the experiment.

Literature Cited

(1) Kuenen, J. P.; Robson, W. G. The Mutual Solubility of Liquids. *Philos. Mag.* **1899**, *48*, 180–203.
(2) Tanaka, H.; Kato, M. Vapor–Liquid Equilibrium Properties of Carbon Dioxide + Ethanol Mixture at High Pressures. *J. Chem. Eng. Jpn.* **1995**, *28*, 263–266.
(3) Ishihara, K.; Tsukajima, A.; Tanaka, H.; Kato, M.; Sako, T.; Sato, M.; Hakuta, T. Vapor–Liquid Equilibrium for Carbon Dioxide + 1-Butanol at High Pressure. *J. Chem. Eng. Data* **1996**, *41*, 324–325.
(4) Ishihara, K.; Tanaka, H.; Kato, M. Phase Equilibrium Properties of Ethane + Methanol System at 298.15 K. *Fluid Phase Equilib.* **1998**, *144*, 131–136.
(5) Kato, M.; Tanaka, H.; Yoshikawa, H. High-Pressure Phase Equilibrium for Ethane + Ethanol at 311.15 K. *J. Chem. Eng. Data* **1999**, *44*, 116–117.
(6) Kodama, D.; Tanaka, H.; Kato, M. High-Pressure Phase Equilibrium for Ethane + 1-Propanol at 314.15 K. *J. Chem. Eng. Data* **2001**, *46*, 1280–1282.
(7) Soave, G. Equilibrium Constants from a Modified Redlich–Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
(8) Kato, M.; Tanaka, H. A New Three-Parameter Pseudo-Cubic Equation of State. *Adv. Cryog. Eng.* **1986**, *31*, 1169–1179.
(9) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Received for review December 13, 2001. Accepted May 15, 2002. A research grant of the College of Engineering, Nihon University, was given to D.K.

JE010324I